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c) 1-10 % of at least one surfactant belonging to the class of

c) quaternary ethoxylated ammonium saits.

a) ethoxylated amines: b) ethoxylated diamines; and

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## DRILLING FLUID

The invention relates to a drilling fluid comprising a stacle cill in water emulsion consisting of

- a) 50-96 \*-v aqueous phase
- b) 3-40 %v oil chase
- c) 1-10 %v of at least one surfactant belonging to the class (a) of ethoxylated amines having the
- s formula:

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in which R is any hydrophobic organic group and x and y are integers >1, the sum of which is in the range of from 4-20, and or to the class (b) of ethoxylated diamines having the formula:

in which R is any hydrophobic organic group, x, y and z are integers 1, the sum of which is in the range of from 4 to 20 and n is an integer in range of from 1 to 6, and/or to the class (c) of quaternary ethoxylated ammonium salts having the formula:

in which R₁ and R₂ are any hydrophobic organic groups, x and y are integers≥1 the sum of which is in the range of from 2 to 20 and A is any anion.

When drilling subterranean wells such as, for example, oil or gas wells, the rotary drilling method is commonly employed. The rotary drilling method utilizes a bit attached to a drill stem, and a drilling fluid or "mud" which is circulated through the drill stem to the bottom of the borehole where it is ejected through small openings in the drill bit. The fluid is then returned to the surface through the annular space between the drill stem and the borehole wall, or casing if one has been installed. Upon reaching the surface, the drilling fluid or "mud" is ordinarily treated to remove cuttings obtained from the borehole, and is then recirculated.

Drilling fluids serve many functions, and should therefore possess a number of desirable physical and rheological properties. For example, the viscosity of a drilling fluid should be sufficient to permit it to effectively transport bit cuttings from the bottom of the borehole to the surface for removal. A drilling fluid should also prevent excessive amounts of fluid from flowing from the borehole into surrounding formations by depositing on the wall of the hole a thin but substantially impervious filter cake. In addition, a drilling fluid should be able to hold solids in suspension, preventing their return to the bottom of the hole when the circulation is reduced or temporarily interrupted. This property can be obtained by utilizing additives which will impart a get structure to the drilling fluid to increase viscosities. The get structure, however, is preferably such that cuttings can be removed from the drilling fluid by passing the fluid through filtration equipment such as a shale shaker and or sand cyclones prior to recirculating the fluid to the drill bit. A drilling fluid must also exert pressure on the surrounding formations, thus preventing possible collabse of

the borehole or influx of highly pressurized oil or gas in the formation. Finally, a drilling fluid should serve as a lubricating and cooling agent for the drill string and the bit.

Drilling of easily dispersible formations such as shales, marls and chalks often presents a problem in mud solids control. Drilled solids tend to disintegrate in the drilling fluid while being transported to surface s and the fines thus created are very difficult to remove. A build-up of fines is the consequence and leads to an increased viscosity of the drilling fluid and a decreased rate of penetration of the drilling operation. Ultimately mud dilution is required to recondition the mud or drilling fluid.

A method to combat drilled solids disintegration is the application of the drilling fluid according to the invention. This "mud" prevents disintegration of cuttings and so delays the build-up of lines.

In addition the present invention relates to a concept in mud engineering which involves the drilling of a well by the use of an oil in water emulsion which deposits its oil phase onto mineral surfaces. In this manner the interaction of the water phase of the mud and troublesome shale zones is greatly lowered or prevented completely and this facilitates the easy drilling of the well.

A preferred composition of the mud system according to the invention is as follows:

a) 87-93 %v aqueous phase

b) 4-8 %v oil phase

c) 3-5 %v surfactant. The heart of the system is the nature of the surfactant interfacial phase, i.e. at least one ethoxylated amine, ethoxylated diamine and/or quaternary ethoxylated ammonium salt which acts 20 both to disperse the oil phase throughout the aqueous phase and also to coat it out onto mineral surfaces. including troublesome shale zones. What distinguishes the present system from those previously existing is the effectiveness of the coating in preventing the undesirable water-shale interactions and the ease with which it is incorporated into typical drilling fluid systems. The ethoxylate amines and diamines and the qualarmery ethoxylated ammonium salts are essential for the present drilling fluid and none of the surfactants used in the drilling muds according to the existing patent specifications or present in the commercially available systems give as good results as the ethoxylate amines and diamines and the quaternary ethoxylcted ammonium salts.

The ethoxylated arnines and diamines are commercially available surfactants with the following chemical formulas, respectively:

and

The "R" group may be any hydrophobic organic group, aliphatic or aromatic, saturated or unsaturated, straight chained or branched and a preferred set of groups are those derived from tallow, olive oil or coconut oil. The number of ethylene oxide units is chosen to balance the particular hydrophobic group in any particular case and hence provide the desireable emulsification and wetting properties. When the "R" group is derived from tallow, the preferred number of ethylene oxide groups is a proximately 15, but this can vary considerably depending upon the expected conditions of use. For low or moderate temperatures, approximately 5 units will suffice and in conditions of very high temperatures or very high salinity, more than 15 may be necessary. The integer n is preferably 3.

The quaternary ethoxylated ammonium salts are also produced on a commercial scale. They are surfactants with the chemical formula:

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The "Ri" and "Ri" groups may be any hydrophobic organic groups, alignatic or aromatic, saturated or unsaturated, straight chained or branched. A preferred set of groups are those derived from tailour occordi to loil or olive oil. The "R<sub>2</sub>" group is more preferably a methyl group. The number of atoy and course and a single the range of from 2 to 20. When the "Riff group is derived from tallow and the "Riff group is a main, i group the preferred number of ethylene oxide groups about 15, but this can vary decending upon the conditions of use. The Attsymbolizes any inorganic or organic anion, but in actual practice A impostly recresents the chloride anion.

These surfactants form stable oil in water emulsions over a wide composition range. for example 75% water phase 20% oil phase 5% surfactant

50% water phase/40% oil phase/10% surfactant

These compositions are intended to be illustrative and not exhaustive and the exact one chosen for any particular application will depend upon the exact nature of the problem. Obviously, for both environmental and cost considerations the minimum dilisurfactant phase necessary to effectively coat the welfore and cuttings surfaces is desirable but balanced by the need to maintain the fluid properties without constant new chemicals addition as the well is deepened. This amount must be selected for any given case with a knowledge of the sensitivity of the particular shale being penetrated and of the operating conditions (criting rate etc.) being used. In the laboratory a 90% water phase 6% oil phase 4% surfactant composition has been found to provide good shale inhibition and fluid maintenance properties for two particular shale types tested (Pierre and Hutton shale) but this is in no way the only composition which could be used or even the most desirable in any given field application.

The oil chase is taken to mean any aqueous immiscible fluid which can be successfully emulsified by the surfactant phase and coated out onto mineral surfaces to reduce their interaction with the accepts phase. Examples of these include mineral oils such as diesel or napthenic oils such as Sheilsol DMAE and also vegetable or other natural oils.

The aqueous phase is taken to mean water or any solution in which water is the solvent such as sea water or where electrolytes or other chemicals are deliberately added to achieve or enhance useful fluid properties. To enhance the inhibiting effects of the emulsions in cases of highly swelling shales it is advantageous to add 1-15 per cent of a potassium sait such as potassium chloride to the water base

To be useful as a well drilling fluid it is suitable to build certain other properties into such emulsions including desirable rheologies, densities and fluid loss characteristics and these are achieved using the standard technology of mud engineering summarized below.

Desirable meologies are normally obtained using either clay suspensions or dissolved polymers. The ist of possibilities is enormous but generally the common mud viscosifiers such as prenygrated centonite or Xanthan gum have been found to be preferred. These are intended to be advantageous and illustrative examples and not exhaustive and any viscosifier which imparts a useful drilling fluid rheclogy and is compatible with the other system components may be considered.

The variation of fluid density is achieved using the standard technology of mud angineering and usually as by the suspension of high density solids such as barium sulphate in the viscosified fluid. The adjustment of the filtration properties of the emulsions is again carned out using the standard technology of mud engineering by the addition of suspended clays or dissolved polymers such as bentonite, carboxymethy

The invention does not only relate to the formulation of oil in water emulsions which coat out onto shale cellulose or starches etc. or other mineral surfaces bu, also to the incorporation of such an emulsion into a fluid useful for well disting completing and working over, using the standard available mud technology

## Example

The cuttings dispersion test, used to evaluate the interaction between shall cuttings and carricular drilling fluids is carried out as follows:

Shale (in this case Hutton shale from the U.K. North Sea) is ground and sieved and the fraction between

sieves 1.7-2.7 mm is collected and equilibrated with water. Twenty grams of equilibrated shall cuttings is mmersed in 350 mis of the criting fluid and rolled at 50 rpm and 60 degrees centrigrade for 24 nours. After this time the cuttings are collected over a 1.4 mm sieve, washed, dried, re-equilibrated with water and the percentage weight loss of the cuttings calculated. If there was a very large interaction between the fluid and the shall cuttings the shalle will have dispersed into very small particles and hence little will be collected over the 4.6 mm sieve; conversely, if there was little interaction between the shall cuttings and the drilling fluid the cuttings will have largely remained the same dimensions and up to 100% will be culticated.

Thus roiling the cuttings in oure diesel oil results in 100% recovery while rolling in pure water results in 0% recovery and it is therefore concluded that there is little interaction between the diesel oil and the cuttings but a large interaction between the water and the cuttings. All the "real" drilling fluids were evaluated on this scale.

The cuttings dispersion test gives a reasonable idea of the extent of the interaction, chemical and mechanical, between the critting little and the shalle cuttings and has been found in the laboratory to be accurate and reproducible to within 2 per cent.

The results of some cuttings dispersion tests are given below, the higher the percentage recovery the less is the interaction between the shale and the fluid and hence the better the performance of the fluid.

The shale inhibiting drilling fluids were of three types, depending on the surfactant contained therein. They consisted of 90 %v aqueous phase 6 %v oil phase 4 %v surfactant. All three muds used in this example were formulated to have a yield point (= yield value as defined in the book "Composition and properties of oil well drilling fluids" by W.F. Rogers, Gulf Publishing Co. (1953) p. 232) of 15 and were unweighed.

Since sea water is often used as the base aqueous fluid in offshore locations the emulsion muds were compared with each other seawater being the aqueous phase.

25	SURFACIANT TYPE	SHALE TYPE	* RECOVERY
	1) Ethoxylated amine	Hutton	98
	(x+y=15, R derived from	tallow)	
30	2) Ethoxylated diamine	Hutton	98
	(x+y+z=15, n = 3, R deri	ved	
	from tallow)		
	<ol><li>Quaternary ethoxylated</li></ol>	Hutton	99
75	ammonium chloride (x+y=1	5,	
	R <sub>1</sub> is derived from tallo	<i>a</i> ,	
	R, is a methyl group)		
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As a comparative experiment a typical gypsum lignosulphonate mud was tested in the same mainter as described hereinbefore using Hutton snale. The recovery was now only 11%. The superiority of the present systems is clearly demonstrated by the results of the above experiments.

## Claims

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- 1. A drilling fluid comprising a stable oil in water emulsion consisting of
  - a) 50-96 \*• v aqueous phase
  - 5: 3-40 \*ev oil phase
- c) 1-10 fev of at least one surfactant belonging to the class (a) of ethoxylated amines having the tormula.

in which R is any hydrophobic organic group and x and y are integers≥1, the sum of which is in the range of from 4-20, and/or to the class (b) of ethoxylated diamines having the formula:

in which R is any hydrophobic organic group, x, y and z are integers≥1, the sum of which is in the range of from 4 to 20 and n is an integer in range of from 1 to 6, and or to the class (c) of quaternary ethoxylated ammonium salts having the formula:

30 in which R₁ and R₂ are any hydrophobic organic groups x and y are integers≥1 the sum of which is in the range of from 2 to 20 and A is any anion.

2. A drilling fluid as claimed in claim 1 in which at least one of the hydrophobic groups R, R<sub>1</sub> and R<sub>2</sub> is derived from tallow, coconut oil or olive oil.

3. A drilling fluid as claimed in any one of the preceding claims in which R<sub>2</sub> is a methyl group.

4. A drilling fluid as claimed in any one of the preceding claims in which 4-8 %v oil phase and 3-5 %v surfactant is present.

5. A drilling fluid as claimed in any one of the preceding claims in which in the aqueous phase from 1 to 15 %wt of a potassium salt is present.

6. A drilling fluid as claimed in any one of the preceding claims in which a clay suspension is present.

7. A drilling fluid as claimed in any of the preceding claims, in which Xanthan gum is present.

8. A drilling fluid as claimed in any of the preceding claims in which n = 3.

 A drilling fluid as claimed in claim 1, substantially as described hereinbefore with special reference to the Example.

10. A process for drilling, completing or working over a well in an underground formation in which as process a drilling fluid as claimed in any one or more of the preceding claims is circulated.

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